Effect of current density on the electron microprobe analysis of alkali aluminosilicate glasses

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ABSTRACT

In a previous work (Morgan and London 1996), we proposed an optimized procedure for electron microprobe analysis (EMPA) of rhyolitic glasses using a broad (20 μm diameter), low-current (2 nA) fixed beam. Some important applications for EMPA of glass, such as vitreous inclusions in minerals and experimental run products, require smaller beam diameters that produce greater areal current densities (expressed as nA/μm^2). For these situations, we have assessed the effect of areal current density on the migration of Na and its concomitant effects on other elements and their ratios during EMPA of granitic glasses. Anhydrous and hydrous glasses of a haplogranite composition (Ab$_{38.23}$Or$_{29.31}$Qtz$_{33.37}$C$_{0.10}$) were analyzed at 20 kV accelerating potential, using 2–50 nA beam currents, fixed beam diameters of 2–20 μm, and counting times scaled to yield similar analytical uncertainty at each condition (~2.6% relative for Na$_2$O). There is almost no loss of Na ($\leq$1.7–2.7% relative) using a current density of 0.006 nA/μm^2, minor (7–9%) Na loss for current densities up to 0.1 nA/μm^2, and increasing Na loss with higher current densities that becomes severe at >0.5 nA/μm^2 (e.g., 48–63% relative loss from hydrous glass at 50 nA and 2 μm during 3–6 s of irradiation). Sodium migration is more pronounced in hydrous glasses than in anhydrous ones, with significant loss from hydrous glass occurring during the first second of irradiation. The migration of Na results in increased concentrations of Al and Si, but little or no change in the concentration of K; if not fully corrected for, these effects produce systematic errors in important elemental ratios. With current densities <0.01 nA/μm^2, anhydrous glasses or crystalline materials are suitable standards and data correction may not be needed. Significant Na loss using current densities up to ~0.1–0.2 nA/μm^2, especially in hydrous glasses, requires data correction or primary standardization utilizing a glass having composition and water content similar to the unknown. Current densities $\geq$0.5–1.0 nA/μm^2 are not suitable for EMPA of glass because of large and uncertain corrections (~25% to >100% of the Na$_2$O value obtained).

The correlation of analytical condition (beam current and diameter) with current density and EMPA results provided here allows analysts to select beam conditions that optimize the quality of analyses. When current densities >~ 0.01 nA/μm^2 must be used (e.g., with beam spot sizes <20 μm), the results can lead to improved estimates of the systematic errors due to alkali migration. Natural and some experimental glasses contain a variety of other minor components among which Ca and Fe are important, and so the discussion of analytical methods is extended to more complex compositions. For example, Na migration is accelerated as glass structures become less polymerized than those of simple tectosilicate stoichiometry (e.g., due to increasing alkalinity and/or the presence of fluxing components such as F, Cl, B). Analysis using 20 kV accelerating voltage, as opposed to 15 kV, both slightly decreases Na migration and improves limits of detection and statistical accuracies for minor components such as Fe while providing reasonable beam penetration depths.

INTRODUCTION

Sodium migration out of the beam excitation volume during electron microprobe analysis (EMPA) of silicate glasses has been recognized and studied for decades (e.g., Lineweaver 1962; Varshneya et al. 1966; Borom and Hanneman 1967; Vassamillet and Caldwell 1969; Kushiro 1972; Goodhew and Gulley 1974; Goodhew 1975; Watkins et al. 1978; Jercinovic and Keil 1988; Nielsen et al. 1995; Spray and Rae 1995; Hanson et al. 1996; Morgan and London 1996). Concomitant with the loss of Na, X-ray intensities and resultant concentrations of comparatively immobile major elements including Si, Al, K, and (in some cases)

Ca increase. The migration of Na out of the X-ray excitation volume is enabled by local heating accompanying the flux of beam energy into the sample (Vassamillet and Caldwell 1969), and thus current density (current per unit area of sample irradiated, expressed herein as nA/μm^2) likely is the most important factor in controlling the mobility of Na. Cryogenic (e.g., Nielsen and Sigurdsson 1981) and intermittent count-and-wait methods have been applied to eliminate or reduce sample heating, but such methods commonly are either not available or not efficient for routine analysis with most combinations of microprobe hardware and software. Hence, the analyst is left with the tasks of minimizing and/or correcting for the effects of Na migration. Although the effects of beam current and/or current density on glass analysis have been presented in studies such as those mentioned above,

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application of this knowledge has been hindered by the lack of a simple, systematic demonstrated relationship between analytical condition (beam current and diameter) and EMPA result. Moreover, most of the correction methods applied to date (e.g., Nielsen and Sigurdsson 1981) are derived from analysis of anhydrous glass standards although Morgan and London (1996) pointed out that Na migration is more rapid and extreme in hydrous glasses than in anhydrous ones. In Morgan and London (1996), we examined the effect of beam current on analytical accuracy with hydrous and anhydrous granitic glasses using only broad, defocused beams (~20 μm diameter), and we proposed an analytical procedure to minimize the effects of beam damage and the consequent corrections. This new study goes an important step further by considering changes in elemental concentrations as a function of the current density, as opposed to beam current only, on the EMPA of an anhydrous and fully hydrated (~6.6 wt% H_2O) granitic glass. The procedure involves analysis of these glasses using beam conditions (currents 2–50 nA; spot diameters 2–20 μm) that span the majority of those previously reported in the literature and/or are currently in use in various laboratories, and provides a systematic correlation between analytical condition (beam current and diameter) and EMPA result.

The first decision to be made for glass analysis is the selection of accelerating voltage. Routine analyses of complex glasses in most laboratories are conducted with accelerating voltages ≥15 kV, because such potentials are required for efficient analysis of Fe using its $K\alpha$ emission (Fe commonly being the heaviest minor element analyzed with a $K\alpha$ emission). A simple review of the literature shows that most laboratories operate at 15 kV, and this is why the study of Morgan and London (1996) was carried out at that potential. Our routine analyses of glasses (including those conducted in this study), however, are conducted at 20 kV primarily because this acceleration maximizes the effect of overvoltage on the production of $K\alpha$ X-ray emissions for Fe and other fourth-row transition metals (nearly doubles the count rate on Fe) while limiting beam penetration depths to ≤2–3 μm for rhyolitic compositions. Accelerating voltages lower than 15 kV are problematic for glass analysis not only due to inefficient excitation of $K\alpha$ emissions from transition metals, but also due to beam damage. The rate of Na migration under the electron beam increases with decreasing accelerating voltage because, at a given beam current, the same flux of electrons will be confined to a shallower penetration depth producing a higher heat flux and greater accompanying temperature gradient within a smaller excitation volume (Vassamillet and Caldwell 1969). Hence, operation at 20 kV, compared to 15 kV, provides an additional advantage in slightly decreasing the rate of Na migration. Accelerating voltages greater than ~20 kV yield no advantages for analysis of most silicic glasses because they provide essentially no increase in excitation of the $K\alpha$ emissions for elements as heavy as Fe. Greater beam penetration depths exceeding 2–3 μm at voltages >20 kV, however, increase the probability of contaminating analyses of glass by irradiation of mineral phases below the surface (e.g., in experimental products or mineral-hosted inclusions). For these reasons, this study is directed at routine analysis of elements with $Z \geq 9$ (F) in silicic glasses using 15–20 kV acceleration.

ANALYTICAL METHODS

Analyses were performed on a granitic glass (Corning Lab Services) made to the nominal composition of the haplogranite minimum at 200 MPa H_2O. Analyses were acquired from both the anhydrous glass and a 3.5 mm diameter glass cylinder equilibrated with excess H_2O in a gold capsule at 800 °C and 200 MPa for 5 days (Table 1). Ongoing investigations of H_2O diffusion in this composition indicate that glass cylinders identical to the one used are completely hydrated and homogeneous after 2–3 days of reaction at 800 °C and 200 MPa. EMPA transects in two directions across the glass cylinder hydrated for five days show no variation in composition or analytical total outside the statistical uncertainty of the analysis, and standard deviations for all elements (as oxide components) are essentially identical between cylinders of the hydrated and the starting (homogenous) anhydrous glasses (Table 1). These observations and the presence of free water in the capsule at the end of the hydration step indicate that the hydrated glass was completely H_2O-saturated at run conditions. Water solubility in metaluminous liquids of similar composition at 800 °C and 200 MPa has been determined to be ~6.2–6.3 wt% H_2O by Karl Fisher titration, with homogeneity verified by FTIR spectroscopy (e.g., Behrens and Jantos 2001; Holtz et al. 2001). EMPA difference methods using 20 kV acceleration, 2 nA beam current, and 20 μm defocused spot yield an H_2O content of ~6.6 wt% for the hydrated glass in this study. Based on reasonable agreement with similar metaluminous compositions, a small normative corundum component in the present glass (which increases water solubility in silicate liquid: Acosta et al. 2003), and comparison of water solubility for this and similar compositions determined by SIMS, FTIR, and EMPA difference (Acosta et al. 2003), we believe this value to be accurate to within 0.5 wt% H_2O and to represent a reasonable starting point by which to compare the effect of analytical condition on H_2O estimation by EMPA difference.

All data were acquired at the University of Oklahoma using a Cameca SX50 electron microprobe equipped with five asynchronous wavelength-dispersive spectrometers. Matrix calculations utilized the PAP algorithm (Pouchou and Pichoir 1985), and oxygen concentration was calculated by stoichiometry with respect to the analyzed elements. Analyses were acquired using 20 kV acceleration; sample currents (measured at the Faraday cup) were 2, 5, 10, 20, and 50 nA; and circular, fixed (not rastered) spot sizes were 2, 5, 10, and 20 μm diameter for each current. For each combination of sample current and spot size, ten point analyses were acquired from clean spots on the same fragments of both hydrous and anhydrous glass. For the main body of this work, analyses were acquired in automated mode (microprobe running from a list of stored point locations) with the $K\alpha$ X-ray intensities of Na (TAP), Al (TAP), and K (PET) acquired first and simultaneously; $SiK\alpha$ was acquired subsequent to Na using the same TAP device. To ensure meaningful comparison, counting times at each beam condition were scaled to yield similar numbers of accumulated counts above mean background and, hence, similar statistical accuracies (i.e., similar standard errors from Poisson statistics: Table 1). Consistent with the methods of Morgan and London (1996), a 30 s counting time was selected at 2 nA current; this represents the maximum counting duration for which migratory loss of Na (≤2%) is less than its relative accuracy (~2.6%) based on counting statistics using a 20 μm beam diameter. Hence, similar statistics were obtained by counting for 12 s at 5 nA, 6 s at 10 nA, 3 s at 20 nA, and 2 s at 50 nA (the latter yielded slightly better theoretical accuracy: Table 1). To assess the potential effect of software counting delays during automated analysis (counting delay after the beam is on the sample), replicate analyses were performed on hydrous glass using a 2 μm spot size at all beam currents in manual (point by point) mode.

RESULTS

Effects on haplogranite components

The calculated current densities (nA/μm^2) as a function of beam current and diameter are shown in Figure 1, and summarized in Table 2. As can be seen from these, current density increases more rapidly as a function of decreasing spot size than as a function of beam current. This relation arises because, although beam current is varied in a linear fashion, irradiation area varies as the square of the spot size radius.

The effects of increasing beam current and decreasing spot size on the measured weight percents of oxide components and two important molecular ratios are shown in Figure 2. As ex-

TABLE 1. Composition of analyzed glasses and calculated EMPA relative accuracies for components in anhydrous glass

	Anhydrous ICP*	Hydrous ICP†	Anhydrous EMPA‡	Hydrous EMPA‡	% R.A. ≤20 nA§	% R.A. 50 nA‖
No. anal.	10	–	50	116		
SiO_2	77.89 (0.29)	72.75	77.95 (0.33)	73.05 (0.31)	0.4	0.4
Al_2O_3	12.73 (0.11)	11.88	12.78 (0.15)	11.79 (0.13)	1.0	0.8
CaO	0.03 (0.01)	0.03	0.02 (0.02)	0.01 (0.01)		
Na_2O	4.50 (0.04)	4.20	4.51 (0.10)	4.12 (0.11)	2.6	2.2
K_2O	4.86 (0.06)	4.54	4.73 (0.11)	4.43 (0.11)	2.1	1.7
Total	100.01 (0.37)	93.40	99.99 (0.45)	93.40 (0.39)		
H_2O	–	6.60	–	6.60		
ASI#	1.005	1.005	1.016	1.016		

Note: Values in parentheses represent 1σ standard deviations.
* Average of 10 analyses by ICP; normalized to account for 0.28 wt% Fe_2O_3 contamination introduced by milling.
† Normalization of ICP analysis to 6.6 wt% H_2O (determined by EMPA difference for hydrated glass).
‡ EMPA using 20 kV acceleration, 2 nA current, 20 mm beam diameter, and 30 s counting times; no corrections applied. Hydrous glass was hydrated for 5 days at 800 °C, 200 MPa (see text).
§ Relative Accuracy (percent) for beam currents ≤20 nA, determined as: $100 \times (1/\sqrt{N})$, where N = number of accumulated counts above mean background; values for all beam currents ≤20 nA are the effectively identical due to scaling of counting times (see text).
‖ Relative Accuracy (percent) for 50 nA beam current, determined as in footnote §.
Aluminum Saturation Index: ≡ mol. $Al_2O_3/(Na_2O + K_2O + CaO)$.
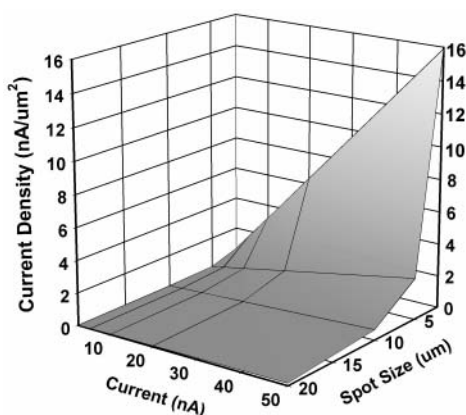
FIGURE 1. Areal current density (nA/μm²) as a function of beam current and spot size.

TABLE 2. Current density (nA/mm²)* as a function of beam current and diameter

	Beam Diameter (mm)			
Beam Current (nA)	2	5	10	20
2	**0.637**	**0.102**	**0.025**	**0.006**
5	**1.592**	**0.255**	**0.064**	**0.016**
10	**3.183**	**0.509**	**0.127**	**0.032**
20	**6.366**	**1.019**	**0.255**	**0.064**
30	9.549	1.528	0.382	0.095
40	12.732	2.037	0.509	0.127
50	**15.915**	**2.546**	**0.637**	**0.159**

Note: Values is bold font were investigated in this study.
* Calculated as current/area of circular spot.

pected, increasing beam current and decreasing spot size lead to progressive loss of Na_2O (Fig. 2a) such that the analytical results mirror the increase in current density (compare Figs. 1 and 2). The effects are more severe in hydrous glass than in anhydrous glass. Because K_2O is a minor component by weight and K is less mobile than Na, increasing current and decreasing spot size lead to little change in its concentration (Fig. 2b). More significant effects of increasing current density are increases in the concentrations of the major components SiO_2 (Fig. 2c) and Al_2O_3 (Fig. 2d). The elemental gains or losses lead to erroneous changes in some important petrogenetic indicators such as K* [≡ mol K/(K + Na): Fig. 2e] and aluminum saturation index (ASI ≡ mol $Al_2O_3/(CaO + Na_2O + K_2O)$: Fig. 2f).

The effect of increasing current density on apparent Na_2O concentration is shown in more detail in Figure 3a, in which changes with increasing beam current are more extreme for the smaller beam diameter. Figures 3b and 3c show directly the effect of increasing current density on Na, with an increasing amount of Na loss from minor (<~3.6% relative loss in anhydrous glass, ~7.4% relative loss in hydrous glass) for current densities less than 0.1 nA/μm², slightly greater (but still <10% relative) loss up to 0.26 nA/μm², and increasingly more dramatic loss of Na for current densities above 0.5 nA/μm² (e.g., >63% relative Na

loss in hydrous glass, ~41% relative loss in anhydrous glass at 15.92 nA/μm²). Based on these results, we recommend analysis at current densities no greater than ~0.1 nA/μm² (<0.06 nA/μm² provides the best results) for which the corresponding beam conditions can be read from Table 2. Changes in composition and resultant uncertainties are so large for current densities ≥0.5 nA/μm², and certainly >1.0 nA/μm², that analysis of even anhydrous samples may not be meaningful.

Effects on H_2O by difference

The effect of beam condition and current density on water by EMPA difference in the raw (uncorrected) data are shown in Figure 4. As can be seen in Figure 4b, values for H_2O by difference are generally within the range considered acceptable for this glass (6.6 ± 0.5 wt%) using current densities up to at least 0.1 nA/μm². There is a slight systematic decrease in values for current densities in the range of 0.1–0.5 nA/μm², and H_2O appears to be underestimated with current densities >0.5 nA/μm².

The effects of counting delay in the automation software

Because the migration of Na under the electron beam is time-dependent, we must consider that there usually is some delay between the time that the beam strikes the sample and the time that the first elements are counted. Such delays arise because: (1) some automation packages utilize a counting delay of one or more seconds after the beam is enabled to stabilize the counting circuitry; (2) in automated mode, the beam may be enabled before the spectrometers have been moved from the last background position counted; and (3) in packages supporting
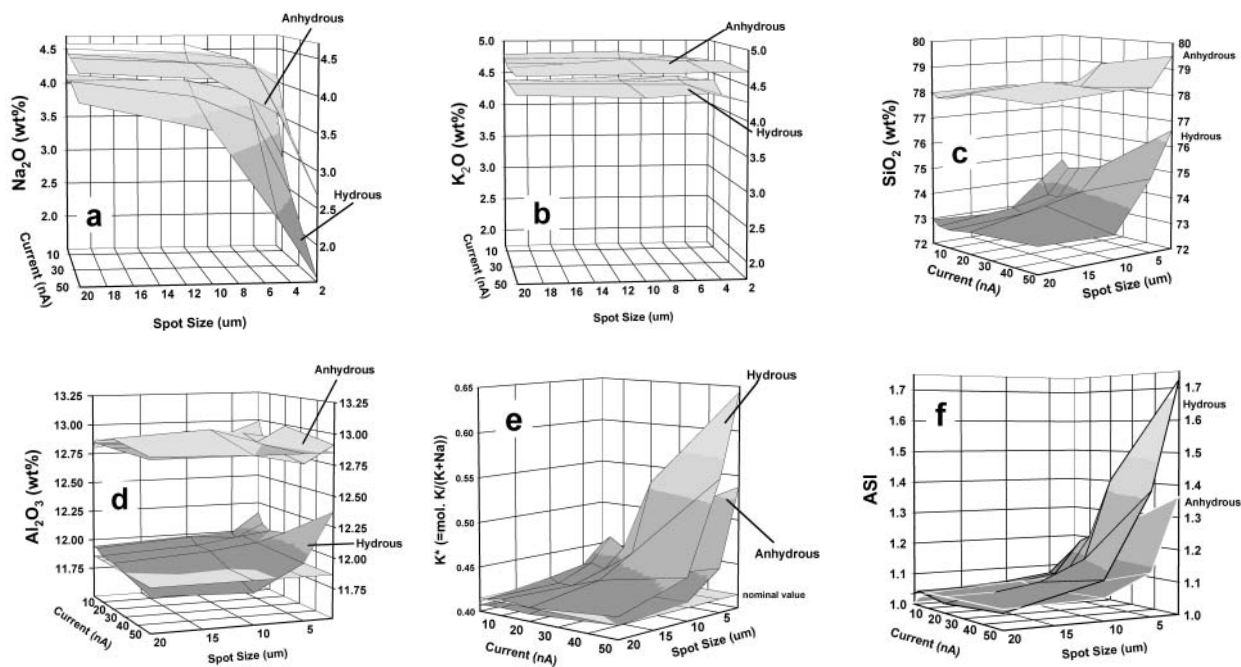
FIGURE 2. Analytical results for oxide components and selected elemental ratios as a function of beam condition. (**a**) Na$_2$O; (**b**) K$_2$O; (**c**) SiO$_2$; (**d**) Al$_2$O$_3$; (**e**) K*; (**f**) ASI [aluminum saturation index, ≡ mol. Al$_2$O$_3$/(CaO + Na$_2$O + K$_2$O)]. Horizontal planes represent nominal values for anhydrous (upper) and hydrous (lower) glass determined from ICP analysis (Table 1).
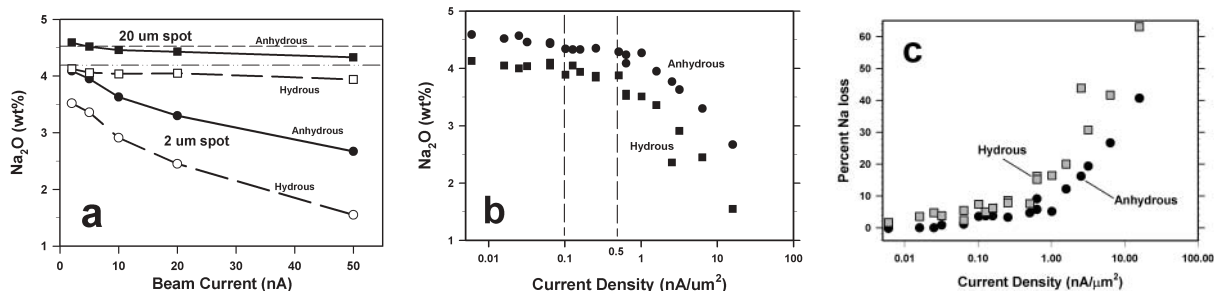

FIGURE 3. Effect of beam condition on Na in granitic glasses. (**a**) Na$_2$O vs. beam current using 2 and 20 μm spot sizes: dashed line = nominal value for anhydrous glass, dash-dot line = nominal value for hydrous glass. (**b**) Na$_2$O vs. aerial beam current density (log scale). (**c**) Percent Na loss vs. areal beam current density (log scale).

asynchronous spectrometer control, the beam will be enabled as soon as the first spectrometer (not necessarily the one used for Na) is in position. If more than one element is assigned to the spectrometer on which Na is counted, and/or that spectrometer is used to analyze more elements than any other spectrometer, there may be additional delay as the spectrometer is moved to the position of the Na$K\alpha$ peak.

The previous data set falls into category 3 above, because Na and Si were acquired with the same spectrometer but only one element was acquired on the others. Manual timing with a stopwatch shows ~4 seconds of irradiation before Na counting began. To help evaluate the potential uncertainties caused by such delays, replicate analyses (using the same counting times as

above) were performed in manual (point by point) mode in which there was no delay for spectrometer movement. This test was performed in the case where Na migration is most extreme—in hydrous glass using a 2 μm spot size. Manual timing shows that there is an ~1 s delay after the beam is enabled before counting begins (case 1, above). The comparison of these results with those acquired in automated mode (Fig. 5) shows that there is relatively little effect of an additional 3 s counting delay at beam currents ≤10 nA (current densities in the range 0.637 to 3.183 nA/μm^2). As expected, the difference between analytical modes increases with increasing current density (6.366 nA/μm^2 at 20 nA, 15.915 nA/μm^2 at 50 nA). Note, however, that all the results using a 2 μm diameter beam spot are systematically low
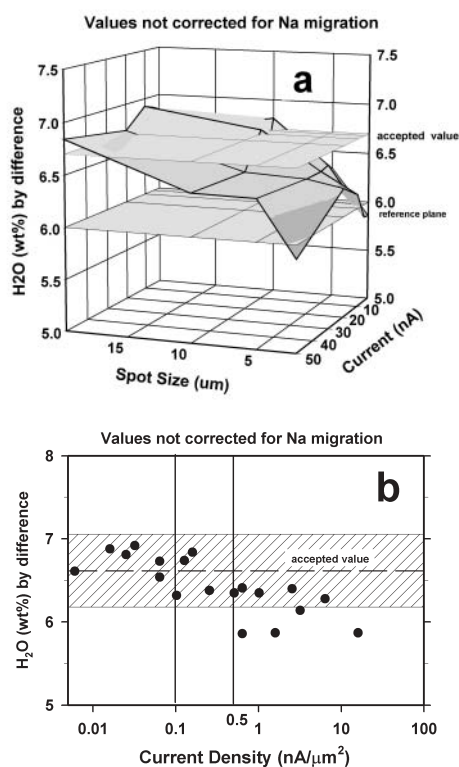
FIGURE 4. Effect of beam condition on H_2O content by EMPA difference method in uncorrected data. (**a**) H_2O as a function of beam condition. (**b**) H_2O as a function of current density (log scale); cross-hatched box represent acceptable range of values as ±0.5 wt% (see text).

FIGURE 5. Comparison of Na_2O values obtained from hydrous glass in manual and automated analytical modes as a function of current density (log scale), to evaluate the effect of counting delays in automation software.

even for currents ≤10 nA, and that at 50 nA, the value with a 1 s delay is only ~0.6 wt% higher (relative) than the value obtained with a 4-second delay in which 2.7 wt% (>63% relative) of Na was lost. These observations support the finding of Morgan and London (1996) that a significant, if not the dominant, proportion of Na loss occurs in hydrous glass during the first second of irradiation. Hence, not only is the effect of counting delay more important at higher current densities, but any perceived gain in statistical accuracy arising from higher count rates is lost as the analyst is faced with the intractable task of trying to hit a rapidly moving target.

DISCUSSION AND RECOMMENDATIONS

The results presented here support the contention that current density is the single most important factor affecting the accuracy of glass analysis by electron microprobe. More accurate analysis will be achieved by methods that eliminate or minimize required corrections and, where required, by correction methods that are appropriate to the analytical conditions and sample composition. The present study is intended to assist analysts in the selection of beam conditions (spot size and beam current) that optimize the quality of the EMPA. The results could be used to correct systematic errors in some cases, but with the following important caveats. First, we emphasize that these results cannot be applied to micr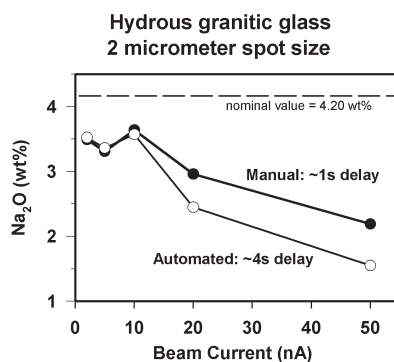oprobe analysis of glasses with substantially different compositions; the results are applicable only to simple granitic compositions, and cannot be rigorously used for correction of compositions involving significant differences in alkalinity (ASI < 1.0) or concentrations of non-aluminosilicate components (e.g., F, P, B, Cl, etc). Second, we note that the magnitudes and rates of Na loss observed in this study at 20 kV likely are not quantitatively exact for analyses performed at different accelerating voltages (e.g., 15 kV: Goodhew and Gulley 1974). Finally, results and corrections vary slightly between microprobes using similar methods, and may even show small variations between different sessions on a single microprobe due to slight differences in column alignment or beam diameter (the latter affected by age of the final aperture). Hence, truly rigorous correction requires an examination of intensity relations at, or near, the time glasses are analyzed.

Ramifications for data acquisition and correction

Acquisition conditions and the need for correction. We recognize that for many applications, analysis cannot be performed at low enough current densities to eliminate data correction. This is especially true in the cases of melt inclusions and crystal-rich experimental products for which a 20 μm spot, or even a 10 μm spot, is often too broad to be contained within the desired target. As stated above, however, current densities ≤ 0.1 nA/μm² should provide the best results for major elements because any statistical advantage gained by higher count rates at higher current densities is lost by virtue of the large and uncertain corrections arising from rapidly changing composition and counting delays in the software. We recommend analysis of the major components (Na, Al, Si, K, ± Ca) using ≤2 nA beam current, and spot sizes as large as possible (≥5 μm for 2 nA current). Sodium must be counted first and, where possible, Al, Si, and K should be counted simultaneously; if only two TAP devices are available, Na and Al should be counted before Si to minimize effects on calculated values of ASI (Morgan and London 1996). With these methods, reasonable accuracy can be obtained using 30 second counting times for these components (~1.7–2.7% relative for Na). Although improved statistical accuracy might be achieved by increased counting times, the degree to which this can be realized is uncertain because prolonged irradiation

likely will lead to increased Na migration from the analytical volume unless current densities are below the smallest values used here (0.006 nA/μm^2).

We emphasize that the use of current densities $\leq$0.1 nA/μm^2 may not completely negate the need for data correction for hydrous glasses. Using a current density of 0.006 nA/μm^2 (2 nA, 20 μm, 30 s), Na loss in the present hydrous haplogranitic glass is <2% (relative), but for more complex granitic compositions containing ~1 wt% F, we observed 2.5–2.7% loss. Sodium losses of $\leq$ ~2% typically are less than the relative accuracy of the analysis based on counting statistics, so data correction may not be needed (Morgan and London 1996). An increase of current density to 0.102 nA/μm^2 (reducing the diameter of the 2 nA beam from 20 to 5 μm), however, yielded ~7.4% relative Na loss from the present hydrous haplogranitic glass and 17–23% relative loss in more complex, F-bearing, hydrous rhyolitic glasses (e.g., Morgan and London 1996; Morgan et al. 1998). Certainly these latter results require correction for the analyses to have any meaning or relevance.

Importance and estimation of H$_2$O content. Figures 2a, 3a, and 3b showed that Na migration is more rapid in hydrous glass than in anhydrous glass (the slopes of trends for the hydrous glass are steeper), and this difference is exacerbated at higher current densities. This observation requires that if correction is applied by reference to analysis of a standard glass of known composition, the water content of the standard glass should be similar to that of the sample. For example, consider correcting the analyses of the hydrous granitic glass acquired with the two highest current densities investigated in this study. If the (compositionally analogous) anhydrous glass is used as the reference standard for correction, the values for Na$_2$O in the hydrous glass are underestimated by 20–26% relative (0.8–1.1 wt%); i.e., essentially one-fourth of the Na is unaccounted for. Because the dominant proportion of Na migration occurs during the first second of irradiation (the shortest reasonable increment for counting), corrections based on extrapolation to zero-time intensities (e.g., Nielsen and Sigurdsson 1981) also should be derived from analysis of a suitable hydrous glass standard rather than from the unknown (sample), and the effects of counting delays in the software must be accounted for. The use of a hydrous glass standard will permit an assessment of Na loss during the first critical second of analysis, which is not possible for a poorly known sample composition.

The accuracy and utility of estimating the H$_2$O content of glass by EMPA difference from 100%, where oxygen concentration is calculated by stoichiometry with respect to the analyzed elements, is somewhat debated in the literature. The general view is that accuracy and precision with this method are limited to the range of 0.5–1.0 wt% (e.g., Devine et al. 1995; King et al. 2002), with EMPA difference methods generally yielding vales that are too high. Morgan and London (1996), however, demonstrated agreement to within 0.2 wt% for Ab-H$_2$O glasses with H$_2$O contents in the range of ~2.2–9.7 wt% H$_2$O. King et al. (2002) suggested that erroneously high H$_2$O values could result from Na loss from the analytical volume. This explanation seems unlikely because the loss of Na from the excitation volume is offset by increased concentrations of other elements. It has been our experience that the principal inaccuracy in determining H$_2$O

by EMPA difference is overestimation accompanying low analytical totals arising from sample surface imperfections (pitting or poor polish, which can be hidden by carbon coating), improper focus (e.g., drift during automated analysis due to stage heating or change in vacuum), samples not being exactly normal to the beam, and/or sample charging. We maintain that if analyses are conducted carefully, and if the concentrations of all cations are known (including light elements such as Li, Be, B, and other volatile components such as CO$_2$), EMPA difference methods should be accurate to within 10% relative for H$_2$O contents up to ~5 wt%, and to within 0.5 wt% for higher H$_2$O concentrations.

Previously (Fig. 4) we showed that the values of H$_2$O by EMPA difference appear to be optimized using the same values of current density ($\leq$0.1 nA/μm^2) that provide the best results for Na and the other major components. By analogy with the migratory behavior of Na, we can only surmise that water is comparatively immobile under the beam within this range of current densities because sample heating is below its critical diffusion temperature (e.g., Fig. 2 of Spray and Rae 1995). This appears not to be true for current densities >~0.2–0.5 nA/μm^2, as artificially high analytical totals suggest that H$_2$O is driven out of the excitation volume resulting in increased concentrations of the remaining components. Similar to the discussion of Morgan and London (1996), when current densities ~0.01–0.2 nA/μm^2 are required for analysis, the best estimate for H$_2$O by difference is obtained directly from the uncorrected data because Na varies in opposite direction but by nearly equal magnitude to Al plus Si. If post-analysis correction is applied to the data, then Na, Al, and Si must all be corrected; the correction of only Na, and not Si and Al, will lead to a systematic underestimation of H$_2$O by difference.

Other compositional effects. The different behavior of Na among anhydrous haplogranite, hydrous haplogranite, and more complex (e.g., F-bearing) hydrous rhyolitic glasses underscores an important effect of composition. Changes in composition away from the simple haplogranite system that significantly affect the structure of glass, and in particular the structural environment of Na, will change the migratory behavior of Na during analysis (e.g., Fagan 2001). Simple, anhydrous metaluminous granitic glasses have tectosilicate stoichiometry in which Na acts predominantly as a charge-balancing cation associated with tetrahedral Al (Mysen 1983; McMillan and Wolf 1995; Stebbins 1995). Difference in behavior between anhydrous and hydrous haplogranitic glass is likely related to a change in the local environment of Na to a hydrated or hydrolyzed complex in the vicinity of Al upon hydration (e.g., Schmidt et al. 2001; Kubicki and Sykes 2004). No difference in Na loss is observed between metaluminous and peraluminous compositions of similar H$_2$O content, and none should be expected because increasing aluminosity should not change the local environment of Na. Sodium loss will be more extreme in peralkaline compositions because some fraction of Na forms a more mobile, terminal species on non-bridging O atoms associated with Si (Mysen 1983; McMillan and Wolf 1995). The differences in Na loss observed between simple hydrous haplogranite glass and the more complex rhyolitic glasses discussed previously are probably, at least in part, related to the effects of F. Fluorine is known to form Na-Al-F complexes that may depolymerize rhyolitic liquids/glasses

(Mysen and Virgo 1985; Kohn et al. 1991; Schaller et al. 1992), and the complex vitrophyres examined contained 0.3–1.1 wt% F (Morgan and London 1996; Morgan et al. 1998). Although similar effects may be expected by the presence of other non-aluminosilicate components that may form complexes with Na (e.g., P: Cody et al. 2001), there is no structural reason to assume that minor abundances of the common, normally octahedral, network-modifying cations (e.g., Fe^{2+}, Mg, Mn, etc.) will have any impact on Na migration behavior. In total, however, these considerations suggest that if correction to the data is necessary, the standard glass used should have similar composition in terms of alkalinity/aluminosity, water content, and fluxing/depolymerizing components (e.g., F, P, and perhaps Cl, B).

Correction procedures. For truly rigorous correction, intensity corrections should be applied prior to ZAF matrix calculations (Spray and Rae 1995). This method, however, commonly is not feasible for many researchers who have limited access to the microprobe or appropriate software, and/or receive data containing only the element/oxide concentrations (and not intensity data) for both samples and standards. For the latter case, reasonable results can be obtained for the major elements by direct correction of element or oxide concentrations in a spreadsheet using correction factors obtained from a ratio between analyzed and known concentrations for suitable glass standards (we suggest placing the corrected values in a new set of columns, so that the original, raw, data is not lost). If molecular formulae are to be calculated from the EMPA, note that the same correction factors cannot be applied to oxide and cation (formulae) values. Differences in elemental mass and oxygen stoichiometry among the cations of the major oxide components make the corrections based on concentration inappropriate for recalculating molecular formulae. Either the molecular formulae for the corrected EMPA must be recalculated, or else separate correction factors for the cations (on an equivalent oxygen basis) can be derived from analysis of the standard glass. To date we have noted no difference in cation results between these latter two methods to three significant figures (0.00× apfu).

Ramifications for standard materials

An important benefit of using low current densities lies in the greater availability and versatility of suitable standard materials. Morgan and London (1996) noted that with the lowest current density used in this study (~0.006 nA/μm^2), reasonable results (within the statistical uncertainty of the analysis) can be obtained using anhydrous crystalline or glassy materials as the standards for analyzing metaluminous glasses containing up to 10 wt% H_2O. Following from the discussion above, these methods also work well for hydrous peraluminous compositions. The analysis of alkaline compositions at all current densities, presence of fluxing components, and the use of higher current densities in hydrous metaluminous to peraluminous compositions, however, place additional demands for glassy materials for use as either primary or secondary standards, the latter for constraining correction parameters as discussed in the preceding section. Hydrous glass standards need to be re-polished and or replaced periodically, because they are known to at least partially degas their H_2O contents over periods of weeks to years (e.g., King et al. 2002), especially if held under high vacuum.

Recommendations for more complex compositions

Low count rates make the use of very low current densities ineffective for the analysis of minor to trace level components in glass. Fortunately, the haplogranite components (Na_2O, K_2O, Al_2O_3, SiO_2) plus H_2O and CaO constitute ≥98 wt% of most natural rhyolitic to andesitic glasses. Due to their minor abundances and generally immobile nature, the results for other commonly analyzed elements such as Mg, Fe, Mn, Ti, etc. will not be strongly affected by Na migration. Therefore, more complex compositions can be analyzed using multiple beam conditions (Morgan and London 1996): an initial beam condition of low current density for Na, K, Al, Si, ± Ca (as described above), followed by a beam condition with higher current density for the remaining elements (20–50 nA current with the same spot size, counting times scaled as needed for detection sensitivity). Calcium may be analyzed at either condition, but probably should be analyzed at the second condition if the CaO concentration is less than a few tenths of weight percent. Most modern microprobe automation packages (standard automation on all JEOL and Cameca instruments since the mid- to late-1980s, and some retro-fit packages for older instruments) should support analysis using multiple beam conditions. Although more time consuming than a single condition analysis at higher current, this method provides more reliable results for the major components along with reasonable detection limits for the minor constituents. For cases where automation packages do not support the use of multiple beam conditions, the present results indicate that current densities should not exceed ~0.5–1.0 nA/μm^2 (e.g., diameter ≥5 μm, current ≤10–20 nA: Table 2); such beam conditions approach the upper limit of reasonable migratory behavior for Na (Figs. 3b and 3c) while providing adequate excitation of the minor elements. Even if the major elements are analyzed first, however, such methods will require significant data correction (e.g., ≥ ~6–17% Na loss, depending on composition) or primary calibration using suitable glass standards.

Intra- and inter-sample comparability

A final cautionary consideration pertains to spot sizes used for analyzing populations of melt inclusions of differing size and/or groups of similar experimental products with differing amounts of intergranular glass, especially if one goal of analysis is to evaluate potential heterogeneity within the samples. It may be tempting to analyze different populations of such products by varying the spot diameter to fit the available target sizes. We do not, however, recommend this for current densities greater than ~0.01 nA/μm^2, because different corrections will be required for each spot size and these could mask true differences in composition between populations. Instead, we recommend using only the largest spot size that can be accommodated by all samples/inclusions, so that the corrections applied are the same. Even if this procedure results in some additional analytical uncertainty for one population of samples or inclusions, the relative difference in composition between individual samples or populations is more likely to be preserved.

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